# In situ photolysis of deep ice core contaminants by Çerenkov radiation of cosmic origin

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[1] Ice core contaminants should provide permanent paleoclimatic records if, as it is generally assumed, they remained frozen in place and isolated from sunlight by the reflective overlaying snow layers. The excess CO levels recently detected in 1100–1600 AD Greenland ice core air bubbles relative to their Antarctic counterparts [*Haan and Raynaud*, 1998] amount, however, to an average production of about 5 ± 2 CO molecules $cm^{-3}$ ice $s^{-1}$ in that period. Here we show that such rates are quantitatively consistent with the in situ photodecarbonylation of the chromophoric organic matter present in Greenland, but not in the cleaner Antarctic, ice under the Çerenkov radiation fluxes generated by penetrating muons of cosmic origin. The normal CO levels of modern (1600–1800 AD) Greenland records, and their variability earlier in the last millennium correlate significantly with the occurrence of boreal fires and the associated release of organic aerosol [*Savarino and Legrand*, 1998]. *INDEX TERMS:* 1045 Geochemistry: Low-temperature geochemistry; 1863 Hydrology: Snow and ice (1827); 9315 Information Related to Geographic Region: Arctic region; 9310 Information Related to Geographic Region: Antarctica; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties. **Citation:** Colussi, A. J., and M. R. Hoffmann, In situ photolysis of deep ice core contaminants by Çerenkov radiation of cosmic origin, *Geophys. Res. Lett.*, *30*(4), 1195, doi:10.1029/2002GL016112, 2003.

## 1. Introduction

[2] The reconstruction of paleoatmospheres from the content of ice core air bubbles is crucial to assessing the future impact of anthropogenic emissions on Earth's climate [*Bales and Wolff*, 1995; *Fischer et al.*, 1999; *Legrand and Mayewski*, 1997; *Stauffer*, 2000]. The agreement between Greenland and Antarctic CO, $CO_2$ and $CH_4$ records spanning the last 300 years rules out major interhemispheric gradients [*Fischer et al.*, 1999]. However, CO mixing ratios in older Greenland air bubbles increasingly exceed modern readings (Figure 1), and the constant ($\sim$ 50 ± 4 ppbv) Antarctic levels observed over the last two millennia [*Haan and Raynaud*, 1998]. $CO_2$ data display a similar pattern [*Anklin et al.*, 1995; *Barnola et al.*, 1995; *Tschumi and Stauffer*, 2000]. Both phenomena imply in situ chemical processing, and signal the onset of significant contamination in Greenland ice sections deeper than $\sim$155 m by species [*Savarino and Legrand*, 1998] that slowly release CO and $CO_2$ by unspecified mechanisms. These observations challenge the generalized premise that chemical activity is permanently arrested in deep ice cores, and pose a genuine problem.

[3] Since excess $CO_2$ could partially arise from the slow acidification of widespread carbonates, and since Greenland ice is verifiably contaminated with higher levels of organic matter than the Antarctic pole cap [*Kawamura et al.*, 2001; *Petit et al.*, 1999], surplus CO is a more direct expression of the chemical transformations undergone by organic precursors in glacial environments. The fact that many ice core sections are acidic and contain carbonates, generic organic material and oxidizing agents in close proximity after hundreds of years reveals that mere reagent availability is an insufficient condition for reaction. Impurities only react upon encounter, an infrequent event controlled by the exceedingly small concentration gradients and molecular mobilities prevalent in microcrystalline ice matrices. In contrast, photochemical transformations are unimolecular processes not subject to substrate distribution or temperature effects. The photochemically active organic matter present in snow and deep ice is chemically similar to [*Calace et al.*, 2001], or derives from the colored organic matter globally found in atmospheric aerosol [*Bales and Wolff*, 1995; *Fuzzi et al.*, 2001], rivers [*Gao and Zepp*, 1998], lakes [*Zuo and Jones*, 1997] and oceans [*Mopper et al.*, 1991], which is known to release CO upon illumination [*Johannessen and Miller*, 2001; *Miller et al.*, 2002; *Moran and Zepp*, 1997; *Valentine and Zepp*, 1993]. However, the possibility of photochemistry in deep ice has been discounted, due to the high reflectivity of the snow cover to ultraviolet sunlight [*Gerland et al.*, 1999; *Glendinning and Morris*, 1999], and the lack of a conceivable source of in situ actinic radiation. Still, "even the highly improbable must be considered over the long timescales involved in ice core chemistry. Organic acids and other C-containing species present in sufficient quantities have the potential to influence CO and $CO_2$ values, if a reasonable mechanism were proposed' [*Wolff*, 1996]. Here, we show that photochemistry driven by the Çerenkov radiation continuously emitted within deep ice cores by relativistic muons of cosmic origin is the "reasonable mechanism' underlying excessive CO in Greenland ice air bubbles.

## 2. Background

[4] About $F$ = 0.01 energetic (kinetic energy $T > 0.1$ GeV) muons $cm^{-2}$ $s^{-1}$ continuously hit the Earth's surface [*Thompson*, 1973]. Relativistic charged particles, such as muons, moving at speeds $v$ larger than the speed of light in ice $v_i$ induce a macroscopic polarization field about a plane perpendicular to their trajectory, because the perturbed medium cannot maintain instantaneous electroneutrality. Relaxation of the transient polarization behind the muon leads to the emission of continuous Çerenkov radiation. For


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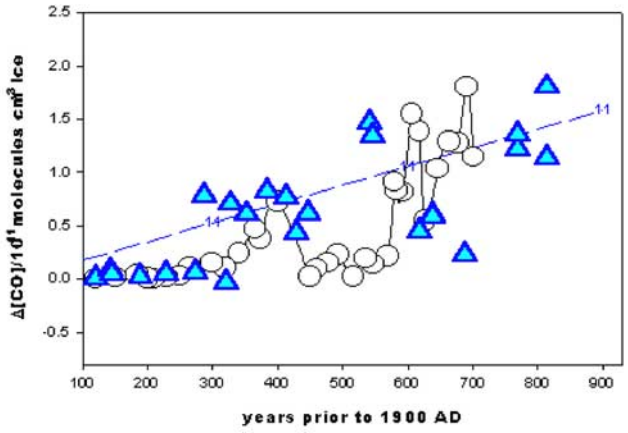


**Figure 1.** Δ: The difference of CO concentrations Δ[CO] (in $10^{11}$ molecules $cm^{-3}$ ice) between Greenland ice bubbles formed before and after 1640 AD [*Haan and Raynaud*, 1998], as function of age. Modern baseline CO concentrations comprise data for the period 1640–1880 AD (see text). A linear regression to the data (not shown) has a slope = $(1.51 \pm 0.6) \times 10^8$ molecules $cm^{-3}$ ice $yr^{-1}$. Dashed line: calculated from equation (8) for the organic matter concentration in ice cores reported by Kawamura et al. [*Kawamura et al.*, 2001], and the dust content of Antarctic ice reported by Askebjer et al. [*Askebjer et al.*, 1997]. ○: The function [FI × age] vs age. FI is the fire index data reported by Savarino and Legrand [*Savarino and Legrand*, 1998].

ice, having a refractive index of $n \sim 1.32$ over most of the UV spectral region: $v_i = c/n = 0.756\ c$. Since:

$$\nu/c = \beta = \sqrt{1 - \frac{1}{[1 + (T/m_o c^2)]^2}} \qquad (1)$$

muons with $m_o c^2 = 105$ MeV, $T > 0.1$ GeV, have speeds $\nu > 1.32\ \nu_i$, and are, therefore, Çerenkov-active. The fundamental equation of the Çerenkov effect [*Jelley*, 1958]:

$$\frac{dN}{d\lambda} = -2\pi\gamma\left(1 + \frac{1}{\beta^2 n^2}\right)\frac{1}{\lambda^2} \qquad (2)$$

(where $\gamma = e^2/ = c = 1/137$) yields the number of photons $dN$ emitted by each muon between $[\lambda \pm d\lambda]$ per cm of their tracks. An integral flux of $F = 0.01$ muons $cm^{-2}\ s^{-1}$ will therefore generate $dR_{Cerenkov} = 1930\ \lambda^{-2} d\lambda$ photons $cm^{-3}\ s^{-1}\ nm^{-1}$ ($\lambda$ in nm throughout) across ice cores. The weakly attenuated muons will travel hundreds of meters in ice before their kinetic energies drop below the Çerenkov threshold. This mechanism represents a perennial source of short-wavelength photons at all depths, in contrast with solar radiation at sea level whose spectrum is strongly skewed to the red and vanishes below 300 nm.

[5] The photodegradation rates of ice dopants depend not only on their light absorption and photochemical properties but also, as we will see, on their concentration and the transparency of the surrounding ice. The optical properties of deep ice in the UV-visible range are now available from the AMANDA project, which involves the detection of Çerenkov radiation emitted by energetic neutrinos ~ 2 km under the South Pole [*Andres et al.*, 2001]. Intrinsic absorption and scattering coefficients of ice were derived from the analysis of photon arrival-time distributions at detectors positioned at various distances from a pulsed, diffuse, monochromatic source [*Askebjer et al.*, 1997]. Scattering is dominated by residual air bubbles, while absorption is due in part to ice itself and, in part, to ice impurities. Photons experience random walks, bouncing specularly at each ice-bubble interface, while being absorbed along their paths. Photon absorption by ice in the near-UV is caused by excitation of $H_2O$ intra- and intermolecular vibrational overtones. Since the probability of multiphoton processes decays exponentially with their multiplicity, absorption coefficients become negligible below 500 nm. On the other hand, the tail of $H_2O$ electronic transitions in the far ultraviolet, the so-called Urbach tail, drops steeply above 200 nm. Photons in the intervening spectral region travel long distances, largely attenuated by the evenly dispersed dust impurities, before reaching localized layers of strongly chromophoric sinks. The following expression encodes the spectral dependence of the absorption coefficient of glacial ice $\alpha(\lambda)$ [*Miocinovic et al.*, 2001]:

$$\alpha(\lambda) = A\exp(-0.482\lambda) + B\exp(-6700/\gamma) + C\lambda^{1.1} \qquad (3)$$

with $A = 8 \times 10^{37}\ cm^{-1}$, $B = 81\ cm^{-1}$. C is proportional to the dust concentration, and has a value of $0.0347\ cm^{-1}$ for the cleanest Antarctic ice.

[6] The organic matter found in ice cores is related to that carried by atmospheric aerosol. The dissolved organic matter (DOM) in fog water is acidic and polyfunctional, absorbs light in the 200–450 nm range, and comprises dialkyl ketones and diketones, alkanedioic acids, hydroxyalkanoic acids, and macromolecular polycarboxylic acids such as fulvic acid, which are analogous to the species recently detected in Antarctic snow and ice [*Calace et al.*, 2001; *Fuzzi et al.*, 2001]. More specifically, a series of homologous α,ω-dicarboxylic acids, ketoacids, and dicarbonyls were characterized in Greenland ice core samples (206 m deep, 450 years old) [Kawamura et al., 2001]. However, they amount to only about 5% of the total organic carbon content of ice: [TOC] = $(1.8 \pm 1.0)$ μg TOC $g^{-1}$ ice = $(1.7 \pm 0.9)$ μg C $cm^{-3}$ ice (ice density $\delta = 0.916\ g\ cm^{-3}$). The remainder is deemed to consist of the DOM found in natural aquatic environments, and in soil. However, TOC levels varied considerably over the last millennium. A high-resolution study of the organic matter collected at Summit in central Greenland since 1193 AD reveals the occurrence of sharp spikes in formate and oxalate levels, indicative of episodic events supplying TOC. Lacking simultaneous CO and TOC records, we adopted the scaled envelope of such registers, encoded as the index of fire over 1200–1950 AD, as a proxy for TOC (Figure 1) [*Savarino and Legrand*, 1998]. Much less organic material is found in Antarctic ice from the Holocene [*Petit et al.*, 1999]. The absorption cross section ε (base 10) [$cm^2\ g^{-1}$ DOM] of representative DOM at $\lambda \geq 200$ nm was fitted by a gaussian:

$$\varepsilon = 1.39 \times 10^4 \exp\left\{-0.5[(\lambda - 153.5)/115.3]^2\right\} \qquad (4)$$

and increases steeply at shorter wavelengths [*Zuo and Jones*, 1997].

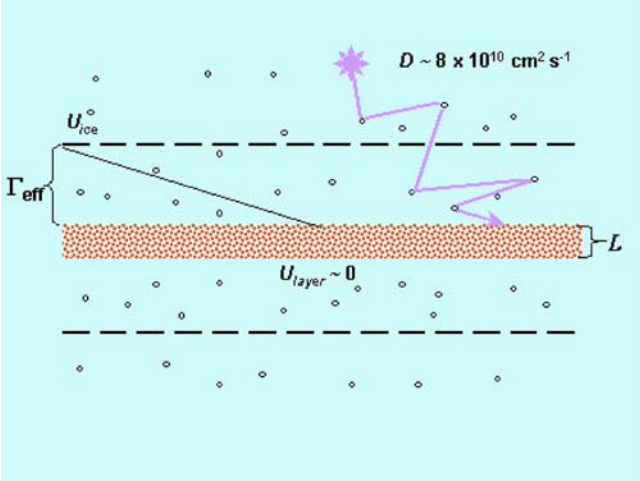


**Figure 2.** Photons created over the ice core are scattered by gas bubbles, diffusing (photon densities: $U_{ice} \gg U_{layer}$) across depletion zones (thickness $\Gamma_{eff}$) towards the contaminated layer (thickness $L$), where they become absorbed by strongly chromophoric impurities.

[7] It is well established that CO is the main gas-phase product of DOM photodegradation [*Gao and Zepp*, 1998; *Valentine and Zepp*, 1993]. CO formation rates are strongly correlated with DOM concentration, UV absorbance and fluorescence yields. Reductive pre-treatment of DOM with $NaBH_4$, which removes carbonylic functionalities, induces a sharp decrease in photochemical CO production. About 17 low molecular weight species, including: $C_1$-$C_3$ aldehydes, formate, acetate, glyoxalate, levulinate, malonate, and pyruvate, are also identified as photoproducts [*Miller et al.*, 2002; *Moran and Zepp*, 1997]. The presence of soluble iron enhances CO production rates. The quantum yield of CO photoproduction from DOM, $\phi$, decays exponentially with $\lambda$ [*Moran and Zepp*, 1997]:

$$\phi(\lambda) = \exp(-2.68 - 0.020\lambda) \tag{5}$$

The quantum yield for the formation of dissolved inorganic carbon (DIC) in DOM photodecomposition displays a similar spectral dependence, but is about 10 times larger [*Johannessen and Miller*, 2001]. Thus, natural organic matter in ice is expected to be photodegraded into CO, $CO_2$, as well as into simple ketocarbonylic species that may, in turn, undergo a similar fate.

## 3. Rates of Dissolved Organic Matter Photodecarbonylation

[8] The rate of absorption of Çerenkov ultraviolet radiation by thin layers of chromophoric impurities embedded in bubbly, dusty ice cores can be estimated with reference to Figure 2 [*Askebjer et al.*, 1997]. Photon trajectories correspond to random walks having scattering, $\Gamma_s$, and absorption, $\Gamma_a$, lengths. At depths of about 500 m, $\Gamma_s \sim 10$ cm, and the associated diffusion coefficient: $D = \nu_i \Gamma_s/3 = 8 \times 10^{10}$ cm$^2$ s$^{-1}$. For a diffusive process involving attenuation, as in the present case, the average path $l$ travelled by a photon between two points separated by a distance $z$ is given by:

$$l = \frac{\sqrt{3}}{2}\sqrt{\frac{\Gamma_a}{\Gamma_s}}z \tag{6}$$

i.e., $l$ and $z$ are both proportional to $t$, rather than to $t$ and $t^{1/2}$, respectively, as for diffusion in a transparent medium ($\Gamma_a \rightarrow \infty$). Accordingly, photon attenuation, which is proportional to $\exp(-l/\Gamma_a)$, takes place over a scale $\Gamma_{eff} = 2(\Gamma_a \Gamma_s/3)^{1/2}$. For undoped ice: $\Gamma_{a,ice} = 1/\alpha(\lambda) \sim 2 \times 10^4$ cm, $\Gamma_{eff,ice} = 516$ cm at 350 nm. Far away from the absorbing layer (see Figure 2), the average photon lifetime is $\tau = \Gamma_{a,ice}/v_i$, leading to a spectral photon density $dU_{ice} = (\Gamma_{a,ice}/v_i)\, dR_{Çerenkov} = 1930\, (\Gamma_{a,ice}/v_i)\, \lambda^{-2} d\lambda$ photons cm$^{-3}$ nm$^{-1}$.

[9] Enhanced photon absorption by the impurified stratum creates a depletion layer in its vicinity. $\Gamma_{a,layer}$ is given by $1/[\varepsilon(\lambda)\,[DOC])$ that, for the Greenland ice sections, has an average value of $\Gamma_{a,layer} \sim 190$ cm at 350 nm, leading to $\Gamma_{eff,layer} = 50$ cm, $\tau = 50$ ns and, in general, to $dU_{layer} = (\Gamma_{a,layer}/v_i)\, dR_{Çerenkov} = 1930\, (\Gamma_{a,layer}/v_i)\, \lambda^{-2} d\lambda$ photons cm$^{-3}$ nm$^{-1}$ $\ll dU_{ice}$. The spectral photon flux $J_\lambda$ diffusing from bulk ice into the impurified stratum through twin depletion layers of thickness $\Gamma_{eff,layer}$ can be evaluated from:

$$J_\lambda d\lambda = 2D\frac{dU_{ice} - dU_{layer}}{\Gamma_{eff,layer}} \tag{7}$$

The overall rate of CO production (molecules cm$^{-3}$ ice year$^{-1}$) is given by the product $J_\lambda\, \phi(\lambda) d\lambda$ integrated over $[\lambda_1, \lambda_2]$:

$$\frac{d[CO]}{dt} = 4.32 \times 10^{11} \int_{\lambda_1}^{\lambda_2} \frac{\phi}{\lambda^2}\left(\frac{\Gamma_{a,ice} - \Gamma_{a,layer}}{\Gamma_{eff,layer}}\right) d\lambda \tag{8}$$

[10] The integrand in equation 8 typically peaks at $\sim 210$ nm and falls quasi-exponentially with $\lambda$, vanishing above 400 nm. It should be emphasized that the chromophoric material is photochemically processed not only by locally generated photons, but also from those created elsewhere and collected onto the absorbing layer after diffusing through the fairly transparent ice matrix. A strongly absorbing sink acts as an antenna whose collection efficiency is proportional to the ratio $(\Gamma_{a,ice}/\Gamma_{eff,layer})$ and, therefore, depends on dust levels via equation 3, as well as on the chromophore concentration and absorptivity.

[11] The experimental CO mixing ratios in air bubbles from the Eurocore Greenland site antedating 1580 AD were cast as excess CO [*Haan and Raynaud*, 1998], $\Delta$[CO], relative to the constant value of 89.4 ppbv for the period 1640–1870 AD. $\Delta$[CO]'s are plotted vs. age in Figure 1 after converting them into [molecule cm$^{-3}$ ice] units by assuming that the air content of ice is 90 cm$^3$ kg$^{-1}$ice.

[12] Despite the apparent dispersion—due to the intrinsic heterogeneity of the deposits, the analytical difficulties associated with ice sampling and transport, and the variability of TOC levels—there is a significant positive correlation between $\Delta$[CO] and time over a 500 year period. A linear regression of the experimental data $\Delta$[CO] vs. time leads to a slope (not shown in Figure 1) of $(1.51 \pm 0.8) \times$

$10^8$ CO molecules $cm^{-3}$ ice $year^{-1}$. The result of our calculations, based on equation 8 for the combination: {[DOC] = 1.7 μg C $cm^{-3}$ ice; C = 0.0347 $cm^{-1}$} is shown as a dashed line in Figure 1. In Figure 1 we also show the scaled record of the fire index reported by Savarino and Legrand [*Savarino and Legrand*, 1998], which is assumed to represent a proxy for the emission of organic material by biomass burning. Two features deserve comment: the enhanced emissions during the Medieval Warm Period (1200 to 1350 AD), and the dearth of fires during the Little Ice Age (1400 to 1850 AD), with the exception of a cluster of burning episodes about 1450 AD. The high levels of formate, which absorbs weakly in the ultraviolet, in Summit ice from about 120,000 years ago argue against dark reaction pathways as a significant mechanism for ice core record degradation.

[13] It has been proposed that psychrophylic bacteria could possibly metabolise organic material and generate carbon oxides within the interconnected liquid veins of the ice dome above Lake Vostok at depths > 3500 m [*Price*, 2000]. However, since all known microbial communities become dormant below −18 °C [*Rothschild and Mancinelli*, 2001], these bacteria are expected to be inactive at the lower temperatures (< −35 °C) typical of shallower ice core deposits [*Fukazawa et al.*, 1999].

## 4. Summary

[14] The remarkable agreement between estimated and average excess CO data in Figure 1 makes the photodecarbonylation of dissolved organic matter by Çerenkov radiation of cosmic origin the likely source of the anomalous CO levels found in Greenland ice core air bubbles dating from the 2nd millennium AD. The proposed mechanism accounts for the anomaly on the basis of well established phenomena and actual data, without invoking adjustable parameters. The variability superimposed on the secular trend of excess CO apparently tracks boreal biomass burning. The induction of other chemical transformations in deep ice by Çerenkov radiation over geological timeframes remains an intriguing possibility.

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